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PROCESS FOR PREPARING CAST METHYL METHACRYLATE
POLYMERSHEETS

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In casting methacrylate sheets for thermoforming applications, it has heretofore been the practice to add chain transfer agents to the polymerization mix for forming syrup. It has now been found that addition of chain transfer agent can be delayed until after the syrup has been prepared with no loss in thermoformability of sheets prepared from the syrup. Data supplied from the esp@cenet database - Worldwide

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(54) Process for Preparing Cast
Methyl Methacrylate Polymer
Sheets

(57) Thermoformable methyl
methacrylate sheets are prepared by:
(1) polymerizing methyl
methacrylate monomer until 5 to 50
percent by weight of the methyl
methacrylate monomer present has
polymerized,

(2) adding 0.05—1.0% of chain
transfer agent and 0.05—2.0% of
crosslinking agent and

(3) casting in the form of a sheet
and polymerizing remaining monomer
for a time sufficient to obtain a self-
supporting sheet. Delaying the
addition of chain transfer agent until
after the syrup has been prepared
causes no loss in thermoformability of
sheets prepared from the syrup.

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SPECIFICATION

Process for Preparing Cast Methyl Methacrylate Polymer Sheets

Continuously cast acrylic sheet is prepared from methyl methacrylate monomer in two stages. First monomer is partially polymerized to obtain a syrup containing both monomer and polymer.

5 Usually, the syrup contains about 20—30% polymer. The syrup is then cast into sheet form and the polymerization continued. This two stage polymerization is preferred because polymerization in the cast operation proceeds at a faster rate than if polymerization proceeded from a monomer mix alone. 5

Two types of acrylic sheet are prepared by the foregoing procedure. A so-called "general purpose" sheet having a high molecular weight is prepared by carrying out both stages of the polymerization in the absence of a chain transfer agent (i.e., an agent which terminates growth of one polymer chain and starts growth of another chain). The other type of sheet is a so-called "thermoformable" sheet which is prepared by employing a chain transfer agent and a cross-linking agent. The chain transfer agent keeps the molecular weight of the polymer low which is necessary for thermoformability, thus it is added to the monomer mix used to prepare syrup. The cross-linking agent provides a means for obtaining a cross-linked network of high molecular weight and it is ordinarily added to the syrup. 10 15 15

Because the chain transfer agent is present during preparation of the syrup for thermoformable sheets, the syrup cannot then be used to prepare general purpose sheets. Furthermore, the syrup preparation and storage equipment must be cleaned every time it is desired to switch from preparation of syrup for thermoforming sheet to syrup for general purpose sheet. It would be desirable to be able to employ one syrup that could be used to prepare both thermoformable sheet or general purpose sheet. 20 20

Summary of the Invention

It has now been found that the chain transfer agent used in making thermoformable sheet can be added to the syrup, rather than to the monomer mix used to prepare the syrup and that useful thermoformable sheets can still be obtained. Thus, both general purpose sheet and thermoformable sheet can be made from the same syrup and the syrup preparation equipment need not be cleaned after each batch of syrup preparation. 25 25

Specifically, this invention is a process for preparing a thermoformable cast methyl methacrylate polymer sheet which comprises in sequence (1) polymerizing methyl methacrylate monomer until about 5—50 percent by weight of the methyl methacrylate monomer present has polymerized, (2) adding to the polymerizate obtained in step (1) a chain transfer agent in an amount of between about 0.05 and about 1.0 percent by weight of polymerizate, and a cross-linking agent in an amount of between about 0.05 and about 2.0% by weight of polymerizate, (3) casting the mixture of step (2) in the form of a sheet and polymerizing the remaining monomer in the mixture for a time sufficient to obtain a self-supporting sheet. 30 35 35

Description

The function of a chain transfer agent is to limit the molecular weight of a polymer being prepared, while the function of the cross-linking agent is to form a cross-linked network of high molecular weight. Thus, if both are present together during polymerization, it would be expected that the two agents would counteract one another unless a large amount of chain transfer agent were employed compared with cross-linking agent. Surprisingly, however, it was found that the amount of chain transfer agent required in the process of this invention was not greater than the amount that had heretofore been used in the initial polymerization to prepare syrup. 40 40

The monomer mix employed herein contains at least about 80% by weight methyl methacrylate and preferably 100%. When comonomer is present the comonomer can be any ethylenically unsaturated monomer that copolymerizes with methyl methacrylate. Examples of comonomers include other lower alkyl methacrylates or a lower alkyl acrylate or alkylene aromatic comonomers such as styrene. The term "methyl methacrylate polymer" includes copolymers of methyl methacrylate and such comonomers. 45 45

The monomer mix is polymerized by usual procedures to obtain a mixture of about 5—50%, preferably about 15—40% and most preferably about 20—30%, by weight, polymer, with the remainder being substantially monomer. The resulting mixture is commonly referred to as "syrup". Polymerization of the monomer mix is carried out by adding a free-radical initiator and conducting the polymerization at between about 50°C and about 180°C. Pressure is not critical and conveniently autogenous or atmospheric pressure is employed. 50 55 55

The syrup also contains an initiator, such as an azo or peroxide initiator and the like. The syrup can also contain mold release agents, such as stearic acid and the like; or dyes or pigments.

To the syrup so obtained, a chain transfer agent and a cross-linking agent is added. The chain transfer agent is added in an amount to obtain a concentration in the syrup of between about 0.05% and about 1.0% based on weight of syrup; while the concentration of the cross-linking agent added is between about 0.05% and about 2.0% based on weight of syrup. 60 60

The chain transfer agent can be a mercaptan, e.g., alkyl mercaptans of up to 20 carbon atoms,

especially n-alkyl mercaptans of between about 4 and 20 carbon atoms, or aryl mercaptans in which the aryl group can be phenyl or naphthyl and which can contain alkyl (of 1—12 carbon atoms) or halogen (Cl, Br, I) substituents; polyhaloalkanes (preferably of 1—5 carbon atoms); phosphines such as R_2PH or RPH_2 wherein R is aryl of 6—10 carbon atoms, or alkyl of 1—10 carbon atoms.

5 The cross-linking agent can be any organic compound that is copolymerizable with the methyl methacrylate monomer and which contains at least two ethylenically unsaturated double bonds, e.g., a diacrylate or dimethacrylate, such as the alkylene or hydroxy substituted alkylene diacrylates or dimethacrylate, e.g., 1,2-ethylene dimethacrylate or 1,6-hexanediol dimethacrylate.

10 The syrup is cast into a sheet and enough of the monomer remaining in the syrup is polymerized to obtain a self-supporting film. Casting and completion of polymerization is carried out by any of the usual procedures, as for example, by adding initiator and placing the syrup into a mold. The outside of the mold is maintained at between about 50°C and about 100°C by use of a heat transfer medium such as water. A detailed description is found in U.S. 3,872,197.

15 The tensile properties of the thermoformable sheet obtained can be adjusted by varying the amount or the kind of chain transfer agent, the amount of cross-linking agent and by changing the cross-linking agent. Generally increasing the amount of chain transfer agent lowers modulus and tensile strength, but increases ultimate elongation; while increasing the amount of cross-linking agent increases tensile strength, and tensile modulus but lowers the ultimate elongation. The main purpose of the cross-linking agent is to eliminate the "yield point". Presence of a yield point indicates that the sheet is elongating primarily in one area. Such uneven elongation of the sheet results in objects of uneven thickness, which may be undesirable depending on the object desired. While it is difficult to generalize the exact amount of cross-linking agent required, it appears that with the chain transfer agent and cross-linking agent used in the examples, the amount of cross-linking agent present should be at least two-thirds the amount of chain transfer agent present and preferably as much or more of the cross-linking agent should be present. With different chain transfer and cross-linking agents one may expect to find different ratios.

In the examples which follow, viscosity of the syrup obtained was measured with a Brookfield® Model HBT viscometer, No. 2 spindle, spindle rpm 50, and percent polymer in the syrup obtained was estimated from refractive index values of the syrup.

30 The following Examples illustrate the invention.

Example 1

Preparation of Syrup

Methyl methacrylate monomer was partially polymerized by heating at between 80—100°C in the presence of 2,2'-azobis(2,4-dimethylvaleronitrile) initiator. In some preparations dodecyl mercaptan was employed as a chain transfer agent at the beginning of the polymerization.

35 Polymerization was halted after about 5 to 35 minutes of heating at the aforesaid temperature range.

The following syrups were prepared:

Syrup	Methyl Methacrylate Monomer employed	Initiator employed	Minutes of Heating	Dodecyl Mercaptan employed	Syrup Data	
	(g)	(g)		(ml)	B.V. (cps)	% Polymer in syrup
1	1200	0.78	19	0	720	27
2	1076	0.69	<20	0	760	18
3	1200	1.2	20	3.6	740	31

Casting and Completion of Polymerization

100 g of each of the syrups were cast after adding 2,2'-azobis(2,4-dimethylvaleronitrile) initiator dissolved in 4 ml methyl methacrylate (MMA) in an amount of 1% by weight. To syrup 1 was added a chain transfer agent (dodecyl mercaptan) and a cross-linking agent (ethylene dimethacrylate). No additives were added to syrup 2. To syrup 3 was added the cross-linking agent. These syrups were cast between glass plates in casting cells immersed in a water bath (water in the bath was at 70—80°C) and held for 0.5 to 1 hour until polymerization was complete. Completion was measured by cessation of heat evolution. The casting cells were then placed in a 130°C oven for about 1 hour to post-cure the sheets. Tensile bars were cut from the sheets (which were about 1/8 inch thick). The bars were tested in an Instron® at an elongation rate of 571%/minute at 160°C to obtain tensile strength (TS), tensile modulus (TM) and percent elongation (Elong.).

Sheet Preparation

Syrup 1 was cast and polymerized as described immediately above, after adding 0.4 ml dodecyl mercaptan and 0.5 ml 1,2-ethylene dimethacrylate per 100 g of syrup to form Casting Composition

60 1-A. Another 100 g portion of syrup 1 was cast and polymerized as described immediately above, after adding 0.3 ml dodecyl mercaptan and 0.3 ml 1,2-ethylene dimethacrylate to form Casting Composition 1-B. Properties of the compositions are set forth in the table below.

General Purpose Sheet

Syrup 2 was cast and polymerized as described immediately above. No additional additives were added. The resulting sheet is referred to in the table below as General Purpose Composition.

Art Thermoformable Sheet

- 5 Syrup 3 was cast and polymerized as described immediately above, after adding 0.3 ml 1,2-ethylene dimethacrylate to form Art Composition Y. 5

Properties of Art Composition Y are set forth in the table below.

Tensile Properties of Sheets at 160°C, 571%/min Elongation

10		<i>Tensile Strength (psi)</i>	<i>Tensile Modulus (psi)</i>	<i>Ultimate Elongation (%)</i>	10
	Casting Composition 1-A	92	163	304	
	Casting Composition 1-B	114	194	372	
	General Purpose Composition	132	384	134	
15	Art Composition Y	110	218	435	15

Sheets of good thermoformability tend to possess low tensile modulus values and high ultimate elongation values. This combination of properties facilitates handling at thermoforming conditions. It is seen that the art thermoformable sheets of Art Composition Y had a lower tensile modulus value and a higher ultimate elongation value than the sheet of the General Purpose Composition.

- 20 Similarly, it is seen that sheets of Casting Compositions 1-A and 1-B (which were prepared by the process of this invention) both have a tensile modulus value lower than any of the other compositions of the table and have ultimate elongation values higher than that of the sheet of General Purpose Composition. Thus, the value of the process of this invention for preparing thermoformable sheets from a syrup which was prepared in the absence of chain transfer agent and cross-linking agent is evident. 20

25 Example 2 25

Using the procedure for Preparation of Syrup the following syrups were prepared. No chain transfer agent was employed. B.V. means Brookfield Viscosity.

30	<i>Methyl Methacrylate (MMA) Monomer employed</i>	<i>Initiator employed</i>	<i>Syrup Data</i>		30
	<i>Syrup</i>	<i>(g)</i>	<i>B.V. (cps)</i>	<i>% Polymer in syrup</i>	
	A	1200	0.78	720	27
35	B	1000	0.30	960	19
	C	1000	0.30	3900	22
	D	1600	1.04	1820	26

- 336.37 g of syrup A, 387.5 g of syrup B, 505.32 g of syrup C and 1600 g of syrup D were combined. The resulting syrup was then cast and polymerized according to the conditions set forth in the procedure for Casting and Completion of Polymerization, except as noted otherwise in the table below, to obtain a number of thermoformable sheets prepared according to the process of this invention. Both dodecyl mercaptan (DM) and 1,2-ethylene dimethacrylate (EDMA) were added to the syrup. Conditions, additives employed and properties of sheets prepared are recorded in the following table. 40

- 45 Tensile properties were obtained on the Instron® instrument as previously described. "Time to peak" records the time interval from when the cast syrup reaches the water bath temperature to when the maximum temperature is reached, while ΔT at peak is the difference between the maximum temperature and the temperature of the water bath. 45

- 50 In the last 3 runs (numbered 18, 19, and 20) it is seen that the amount of chain transfer agent present exceeds the amount of cross-linking agent present. A yield point was observed in the tensile bars produced from these runs. Thus, in these runs, too much chain transfer agent was present. 50

Casting Syrup, 100 g Syrup Plus

55	<i>Run No.</i>	<i>EDMA, ml</i>	<i>D.M. ml</i>	<i>Initiator, ml 1% Sol. in MMA</i>	<i>Time to Peak (Min.)</i>	<i>ΔT at Peak (°C)</i>	55
	1	0.2	0.1	6	27.8	19	
	2	0.4	0.4	6	44.2	8	

	<i>Run No.</i>	<i>EDMA, ml</i>	<i>D.M. ml</i>	<i>Initiator, ml 1% Sol. in MMA</i>	<i>Time to Peak (Min.)</i>	<i>ΔT at Peak (°C)</i>	
5	3	0.2	0.4	14	21.6	23	5
	4	0.4	0.1	14	13.8	37	
	5	0.3	0.25	10	23.5	20	
	6	0.3	0.25	10	22.6	23	
	7	0.4	0.4	14	21.7	23	
10	8	0.2	0.1	14	13.9	36	10
	9	0.4	0.1	6	23.5	28	
	10	0.3	0.25	10	24.0	21	
	11	0.47	0.25	10	22.0	21	
	12	0.3	0.25	3.3	55.6	5	
15	13	0.3	0.25	16.7	14.2	27	15
	14	0.3	0.25	10	21.1	25	
	15	0.4	0.25	10	20.6	23	
	16	0.55	0.25	10	18.6	30	
	17*	0.40	0.25	10	20.5	23	
20	18	0.2	0.4	6	45.0	9	20
	19	0.3	0.652	10	34.8	11	
	20	0.13	0.25	10	22.8	24	

***Syrup" contained 78.9 g syrup plus 21.1 g color master batch containing pigments, and dispersing agents in acrylic polymer.

	Tensile Properties of Cast Sheet at 160°C					
	<i>Run No.</i>	<i>T.S., psi</i>	<i>T.M., psi</i>	<i>Yield Point</i>	<i>% Elong.</i>	
25	1	141	229	No	408	25
	2	93	174	No	474	
	3	64	133	No	1100+	
	4	149	270	No	249	
	5	113	182	No	969	
30	6	120	188	No	476	30
	7	109	148	No	702	
	8	129	272	No	395	
	9	175	299	No	230	
	10	117	217	No	393	
35	11	140	209	No	312	35
	12	146	207	No	451	
	13	124	177	No	549	
	14	115	186	No	488	
	15	105	181	No	276	
40	16	83Δ	142	No	251	40
	17*	101	130	No	350	
	18	51	108	Yes	1100+	
	19	39	88	Yes	1100+	
	20	85	109	Yes	1100+	

***Syrup" contained 78.9 g syrup plus 21.1 g color master batch containing pigments, and dispersing agents in acrylic polymer.

It is seen that increasing the amount of initiator decreases the "time to peak" while increasing the amount of initiator also increases the "ΔT at peak". If the ΔT is too high the cast sheet may contain voids (believed to be caused by boiling of the monomer). It is important to balance the amount of chain transfer agent, cross-linking agent and initiator used since all three of these appear to have some effect on the "time to peak" and "ΔT at peak". Furthermore, the maximum amount of initiator that can be used and still obtain a void-free sheet will also depend on the rate of heat transfer from the polymerizing sheet to the surroundings.

Thermoformable sheets are useful in preparing molded, shaped articles such as bathtubs, kitchen sinks and the like.

Claims

1. Process for preparing a thermoformable cast methyl methacrylate polymer sheet which comprises, in sequence,

(1) polymerizing methyl methacrylate monomer until 5 to 50 percent by weight of the methyl methacrylate monomer present has polymerized,

(2) adding to the polymerizate obtained in step (1) a chain transfer agent in an amount of 0.05 to 1.0 percent by weight of polymerizate and a cross-linking agent in an amount of 0.05 to 2.0 percent by weight of polymerizate, and

(3) casting the mixture of step (2) in the form of a sheet and polymerizing remaining monomer in the mixture for a time sufficient to obtain a self-supporting sheet.

2. A process according to claim 1, wherein the chain transfer agent is a mercaptan, polyhaloalkane or a phosphine, and the cross-linking agent is an organic compound that is copolymerizable with methyl methacrylate and which contains at least two ethylenically unsaturated double bonds.

3. A process according to claim 1, wherein the chain transfer agent is a mercaptan, and the cross-linking agent is a dimethacrylate.

4. A process according to claim 3, wherein the mercaptan chain transfer agent is an n-alkyl mercaptan of 4 to 20 carbon atoms and the dimethacrylate cross-linking agent is 1,2-ethylene dimethacrylate.

5. A process according to claim 1, 2, 3 or 4, wherein the amount by weight of cross-linking agent is at least two thirds the amount of chain transfer agent.

6. A process according to claim 5 where the amount by weight of cross-linking agent is at least equal to the amount of chain transfer agent.

7. A process according to any one of the preceding claims, wherein step (1) is carried out at a temperature of 50°C to 180°C and wherein the polymerization of step (3) is carried out in a mold in which the outer surface of the mold is maintained at a temperature of 50°C to 100°C.

8. A process according to claim 1 substantially as described in Example 1 or 2.

9. A shaped article obtained by thermoforming a cast sheet prepared by a process as claimed in any one of the preceding claims.